Title: **Pillared Clays as Superior Catalysts for Selective Catalytic Reduction of NO**
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Removal of NO_x (NO + NO_2) from exhaust gases is a challenging task. V_2O_5-based catalysts are commercial catalysts for selective catalytic reduction (SCR) with NH_3 for stationary sources. However, for diesel and lean-burn gasoline engines in vehicles, hydrocarbons would be the preferred reducing agents over NH_3 because of the practical problems associated with the use of NH_3 (i.e., handling and slippage through the reactor). The noble-metal three-way catalysts are not effective under these conditions. The first catalyst found to be active for selective catalytic reduction of NO by hydrocarbons in the presence of excess oxygen was copper exchanged ZSM-5 and other zeolites, reported in 1990 by Iwamoto in Japan and Held et al. in Germany. Although Cu-ZSM-5 is very active and the most intensively studied catalyst, it suffers from severe deactivation in engine tests, mainly due to H_2O and SO_2 .

In the last three annual reports, we reported Cu-exchanged pillared clays as superior SCR catalysts. During the past two years we explored the possibilities with MCM-41, a new member of molecular sieves. MCM-41 shows a regular hexagonal array of uniform pore openings with pore dimensions between 1.5 and 10 nm. Because it has high thermal stability, high BET surface areas and large pore volumes, MCM-41 has already attracted considerable interests in recent years. It has been studied as catalysts, support and sorbents. In this work, we investigated the activity of Cu-exchanged pillared clay, noble metal doped Al-MCM-41 and Rh-exchanged Al-MCM-41 catalysts in SCR of NO with propylene in the presence of excess oxygen. Some results are summarized in Table 1.

The SCR of NO by ethylene was first investigated on copper ion-exchanged Al_2O_3-Laponite. Cu^{2+}-exchanged delaminated Al_2O_3-pillared laponite clay was much more active than Cu-ZSM-5 and Cu-TiO_2-PILC under the same reaction conditions. The maximum turnover frequencies (TOF = mmol of NO converted per Cu ion per hour) are as follows: 46 for Cu-Al_2O_3-PILC at 550 ^oC, 21 for Cu-TiO_2-PILC at 300 ^oC and 15 for Cu-ZSM-5 at 300 ^oC. The presence of H_2O and SO_2 only decreased the SCR activity slightly for Cu-Al_2O_3-PILC. NO conversion decreased from 82% to 78% at 500 ^oC when 5% H_2O and 500 ppm SO_2 were added to the reaction gases.

Noble metal and transition metal oxide doped MCM-41 catalysts were studied for SCR of NO with C_3H_6 in the presence of excess oxygen. The catalysts had high BET surface areas (> 900 m^2/g) and large pore volumes(> 1.00 cm^3/g). They were very active for the SCR reaction. 60-70 % NO conversion was obtained on the catalysts. The maximum NO reduction rate reached 4.3 mmol/g·h under the conditions of 1000 ppm NO, 1000 ppm C_3H_6, 2% of O_2 and He as balance; but no or little activity was found when CH_4 or C_3H_8 was used. This difference was related to the different nature of these hydrocarbons. The Pt/MCM-41 catalyst showed a good stability. H_2O and

SO_2 did not cause deactivation of the catalyst. MCM-41 provided the highest specific NO reduction rates for Pt as compared with all other supports reported in the literature, i.e., Al_2O_3, SiO_2 and ZSM-5. La and Au promoted Pt/Al-MCM-41 catalysts were better than Pt/MCM-41 for the SCR reaction.

Rh exchanged Al-MCM-41 was studied for SCR of NO by C_3H_6 in the presence of excess oxygen. It showed a high activity in converting NO to N_2 and N_2O at low temperatures. *In situ* FT-IR studies indicated that Rh-NO^+ species (1910-1898 cm^{-1}) was formed on the Rh-Al-MCM-41 catalyst in flowing NO/He, NO+O_2/He and NO+C_3H_6+O_2/He at 100-350 ^oC. This species was quite active in reacting with propylene and/or propylene adspecies (e.g., π-C_3H_5, polyene, etc.) at 250 ^oC in the presence/absence of oxygen, leading to the formation of the isocyanate species (Rh-NCO, at 2174 cm^{-1}), CO and CO_2. Rh-NCO was also detected under reaction conditions. A possible reaction pathway for reduction of NO by C_3H_6 was proposed. In the SCR reaction, Rh-NO^+ and propylene adspecies react to generate the Rh-NCO species, then Rh-NCO reacts with O_2, NO and NO_2 to produce N_2, N_2O and CO_2. Rh-NO^+ and Rh-NCO species are two main intermediates for the SCR reaction on Rh-Al-MCM-41 catalyst.

Table 1 Catalytic performance of pillared clay and MCM-41 catalysts for selective catalytic reduction of NO with hydrocarbons at different temperatures

Catalyst	Temp. (°C)	NO Conv. (%)	NO Conv. to N_2 (%)	NO Conv. to N_2O (%)	C_xH_y Conv. (%)
Cu-Al_2O_3-PILC	350	37.0	37.0	0	-
	400	46.0	46.0	0	-
	450	65.0	65.0	0	-
	500	82.0	82.0	0	-
	550	90.0	90.0	0	-
Pt/MCM-41	200	4.0	2.2	1.8	4.0
	225	8.0	4.4	3.6	10.2
	250	61.0	16.9	44.1	100
	275	49.0	15.2	33.8	100
	300	36.0	11.6	24.4	100
Pt/La-Al-MCM-41	200	5.7	3.0	2.7	6.3
	225	47.1	16.6	30.5	58.3
	250	63.5	19.0	44.5	100
	275	51.9	16.9	35.0	100
	300	38.0	14.3	23.7	100
Pt-Au/Al-MCM-41	200	2.7	2.2	0.5	13.8
	225	16.6	9.3	7.3	100
	250	68.4	25.9	42.5	100
	275	53.7	19.9	33.8	100
	300	38.2	15.8	22.4	100
Rh-Al-MCM-41	250	34.0	20.5	13.5	43.1
	275	68.2	47.1	21.1	100
	300	44.9	29.6	15.3	100
	325	33.5	21.8	11.7	100
	350	23.5	15.7	7.8	100

Conditions: 0.5 g of sample for Cu-Al_2O_3-PILC, 0.1 g for Pt and Rh catalysts, [NO] = 1000 ppm, [C_2H_4] (for Cu) or [C_3H_6] (for Pt, Rh) = 1000 ppm, [O_2] = 2%, He = balance, total flow rate = 250 ml/min.

Publications:

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